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**DIAMOND ELECTRODE AND METHOD FOR PRODUCTION THEREOF**

The invention relates to a diamond electrode with synthetically produced and electrically conductive  
5 (doped) diamonds and to processes for producing it.

Diamond electrodes are distinguished by their high overvoltage for oxygen and hydrogen and are therefore particularly suitable for a wide range of oxidation  
10 processes in aqueous solution. Therefore, possible and particularly interesting applications would be in the field of drinking water treatment (disinfection) and water treatment by anodic oxidation. Further applications include electrochemical synthesis, in  
15 particular the production of oxidizing agents, and electrolysis of water and the electrochemical production of ozone and chlorine.

Currently, diamond electrodes are produced by direct  
20 generation of boron-doped diamond layers on substrate materials, in particular by CVD (chemical vapor deposition) processes. The known techniques differ from one another in particular with regard to the way in which the energy is introduced. In the case of what is  
25 known as hot-filament technology, tungsten wires are heated in a gas mixture of hydrogen, a carbon source and a boron source above a substrate. In this context, it is possible to use various substrates which in the CVD process differ in particular with regard to their  
30 different carbon solubility.

In practice, only copper and gold are inert. Titanium, zirconium, hafnium, niobium, tantalum, chromium, molybdenum, tungsten and silicon form carbide layers  
35 during the coating, which have to reach a certain material-specific thickness (a few nm in the case Si, a few  $\mu\text{m}$  in the case of Ti) before nucleation and therefore diamond deposition occurs. Even longer

starting times during the CVD deposition occur with substrates which dissolve carbon, such as iron, cobalt, nickel, platinum and palladium. At the same time, during the coating reactions occur with the atomic hydrogen and carbon, forming carbide interlayers ( $\text{SiO}_2$ ,  $\text{ZrO}_2$ ). For these reasons, not all metals are equally suitable for coating.

When used as electrodes, it has emerged that various substrate materials which have a low oxygen overvoltage when connected as anode have an insufficiently long service life. If fine cracks are formed in the diamond layer, electrolysis oxygen is immediately formed, and this causes the diamond layer to become detached.

Boron-doped diamond layers produced using microwave plasma (MPCVD) can also be produced without a substrate, so that pure diamond electrodes of very high quality can be produced. To ensure a certain mechanical stability, electrodes of this type have to be produced in a relatively great layer thickness, which causes very high production costs and prevents economic use of this technology.

The invention is based on the object of providing and/or developing diamond electrodes and processes for producing diamond electrodes which make it possible to enable diamond electrodes to be produced at an economically acceptable outlay and accordingly at low cost. Therefore, the intention is for economic use of diamond electrodes to be possible for the first time in a wide range of oxidation processes in aqueous solution. In particular, correspondingly large-area electrodes should be producible, these electrodes being suitable in particular for drinking water treatment or wastewater treatment and/or electrochemical synthesis.

This object is achieved by a diamond electrode designed in accordance with the invention, which has doped

diamond particles embedded in the surface of a metal or metal alloy layer so as to produce an electrically conductive connection to the metal or metal alloy.

- 5 In a process according to the invention for producing diamond electrodes, a powder formed from doped, synthetically produced diamonds is embedded at least in the surface of a metal or a metal alloy, in such a manner as to produce an electrically conductive  
10 connection between the metal or metal alloy and the diamond particles (claim 13).

Therefore, the invention is based on using diamond powder produced on an industrial scale and therefore at  
15 relatively low cost as starting material and connecting it to a metal or a metal alloy so as to produce an electrically conductive connection between the metal and the diamond particles in the form of a diamond electrode. It is known to use industrially produced  
20 diamond powder for various intended applications, for example for abrasive pastes. This diamond powder can also be produced in doped form using one of the standard processes, for example by high-pressure, high-temperature processes using metal catalysts. With these  
25 production techniques, the diamond powder can be made conductive by introducing boron, for example, in the production process.

In the case of an electrode designed in accordance with  
30 the invention, the locations which are left between the diamond particles at the surface of the electrode are provided with a nonconductive oxide layer and are thereby passivated (claim 2). This ensures that the conductivity of the diamond particles is higher than  
35 that of the embedding material and it is impossible for any uncovered metal surfaces to react with the electrolyte solution. In addition, these locations may be provided with a sealing layer, for example a silicate layer (claim 3).

In one preferred embodiment of the invention, the embedding layer is applied to a layer of substrate material which consists in particular of a metal  
5 passivated by oxides or includes such a metal as an alloying constituent or coating (claim 4). Therefore, by way of example, titanium or aluminum and alloys of these metals are suitable. If a mechanically stable material is used for the substrate material, this  
10 material can also be used for contact-connection of the electrode (claim 5). In the case of embodiments of the electrode in which the substrate layer is coated on both sides, or if the rear side is insulated, it is also possible to use other materials (iron, steel,  
15 nonferrous metals, etc.), but also nonconductors (claims 6 and 7).

The embedding layer at least partially comprises elements which are able to form nonconductive oxides  
20 (claim 8). Therefore, inter alia metals or metal alloys selected from the group consisting of magnesium, aluminum, titanium, yttrium, zirconium, hafnium, tantalum, vanadium and zinc are suitable (claim 9).

25 The diamond powder which has been embedded in the surface of the embedding layer is doped in particular with boron, phosphorus or nitrogen and has a grain size of the order of magnitude of 1 to 700  $\mu\text{m}$ , in particular up to 200  $\mu\text{m}$ . It is advantageous to use a diamond  
30 powder with at least substantially coinciding grain sizes (claims 10 to 12).

In a first variant of the process in accordance with the independent patent claim 13, the doped diamond  
35 particles are introduced directly into a substrate material, which contains at least one element which is able to form a nonconductive oxide layer, by mechanical forces and/or the action of temperature (claim 14). This allows inexpensive and rapid production of diamond

electrodes.

One possible way of introducing them by applying mechanical forces consists in the diamond particles  
5 being pressed or rolled into the surface of the substrate material (claim 15).

Another alternative of the process according to the invention in accordance with the independent patent  
10 claim 13 consists in accelerating the doped diamond particles in fluids and thereby introducing them into the surface when they strike the latter (claim 16). This process too is inexpensive and allows simple production of the diamond electrode. Examples of  
15 suitable fluids include water or air, and the acceleration can be effected by means of pumps or compressors.

In a further alternative of the process according to the invention in accordance with claim 13, the doped  
20 diamond particles are mixed with metal or metal alloys which are able to form a nonconductive oxide layer and pressed, so as to produce a pressed part, if appropriate with support plate, which includes the doped diamond particles enclosed in one or more layers  
25 (claim 17). The result, therefore, is an electrode having a plurality of layers of doped diamond particles, so that the ability of the electrode to function is fully retained even in the event of a  
30 certain amount of wear to the latter.

Yet another variant of the process in accordance with claim 13 consists in sintering the doped diamond particles onto substrate materials (claim 18). The  
35 advantage of this process resides in the production of a particularly stable connection between the diamond particles and the substrate material.

In a further process, the metals or metal alloys are

deposited from the vapor phase (claim 19).

In accordance with claim 20, low-melting materials, for example magnesium or a magnesium alloy, which are  
5 melted onto an in particular metallic substrate layer with a higher melting point, can be used as starting material for the embedding layer, the diamond powder already having been mixed with the powder of the alloy or then being applied to the still liquid metal and  
10 finally being cooled.

Yet another variant of the process in accordance with claim 13 provides for a metal or a metal alloy with diamond powder to be deposited by electroplating, with  
15 an aqueous solution or a molten salt, in which the diamond powder is held in suspension by stirring or the like and being incorporated in the deposited metal, being used (claim 21).

20 In accordance with claim 22, the diamond electrodes produced using these processes can be used as starting product for further deposition of doped diamond using conventional processes, in particular CVD and DVD processes.

25 Conductive metals or metal alloys, which at least partially comprise at least one element which is able to form nonconductive oxides, such as magnesium, aluminum, titanium, yttrium, zirconium, hafnium,  
30 tantalum, vanadium or zinc, can be used for the embedding layer and/or the substrate material (claim 23).

In the processes according to the invention, the metal  
35 surfaces or locations which remain clear between the diamond particles are passivated (claim 24). This ensures that the conductivity of the diamond particles is greater than that of the embedding material.

The passivation is effected in particular by producing an oxide layer by means of anodic or chemical oxidation (claim 25).

5 In this case, the anodic oxidation can be carried out by direct current, pulsed direct current or alternating current with the anodic phase period dominating (claim 26). It is simplest to use direct current. Pulsed  
10 direct current allows improved delivery of peroxide forming agents (sulfate, borate) and therefore complete oxidation, on account of the pauses, in which diffusion but no reaction takes place. If alternating current is used, the anodic phase is interrupted by a brief  
15 cathodic phase, with the result that the oxidizing agents are destroyed. They are then reformed in the next anodic phase. This makes it possible to prevent oxidizing agents from penetrating deep into the pores and excessively deep oxidation from occurring. Therefore, a defined layer thickness can be oxidized  
20 without the layers beneath it suffering.

In particular aqueous solutions which contain borate, sulfate, phosphate and fluoride ions in combination are used to carry out the anodic oxidation (claim 27). It  
25 is in this way possible to produce particularly wear-resistant and corrosion-resistant protective layers or oxidation layers.

In a further preferred variant embodiment of the  
30 process, the oxidation solutions are buffered (claim 28). This prevents the solutions from becoming basic and hydroxides, which are water-soluble, also being formed instead of oxides.

35 The pores in the oxide layer may additionally be sealed (claim 29). This increases the mechanical strength and improves the insulation properties. In this context, it is particularly suitable for the surface of the oxide layer to be subsequently treated with an aqueous

silicate which is hardened under air rich in carbon dioxide (claim 30).

Alternatively, sealing can also be achieved by the  
5 surface being transformed by the penetration of  
dissolved metal salts with or without applied  
potential, into a layer with ceramic properties (claim  
31). A treatment of the surface of this type can also  
take place prior to a silicate treatment. In this case,  
10 the ceramic properties can be improved still further in  
a subsequent sintering process. The term ceramic  
properties relates to the stable crystal structures  
which are formed. The sintering process is carried out  
after the additional metals have been introduced into  
15 the oxide layer, with the material being held at a  
temperature around the melting point of the alloy used  
for a prolonged period of time, for example for several  
hours. The elevated temperature results in mobility of  
molecules, which allows the formation of more stable  
20 modifications. In this way, the density, the mechanical  
strength and the thermal stability of the layer can be  
improved.

A further variant according to the invention of the  
25 process as described in claim 13 consists in the doped  
diamond particles being introduced into the surface of  
coated substrate materials, in particular coated with  
Teflon (claim 32). The Teflon layer makes it very easy  
for the gases which are formed when the electrode is  
30 used to be released from the surface of the electrode.

Diamond electrodes produced in this way can be used in  
particular for the production of gases, in particular  
of ozone and/or oxygen (claim 33).

35 The processes according to the invention can be used to  
process diamond powder with a very wide range of grain  
sizes and from various production processes to form  
electrodes. In this context, it is particularly



advantageous to use conductive diamond powder which has a grain size of from 1 to 700  $\mu\text{m}$ , in particular up to 200  $\mu\text{m}$ . The doping is preferably carried out with boron, phosphorus or nitrogen (claims 34 to 36).

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Further features, advantages and details of the invention will now be described in more detail with reference to the drawing, the only figure of which diagrammatically depicts a cross section through an  
10 electrode designed in accordance with the invention.

The diagrammatic embodiment of an electrode 1 designed in accordance with the invention as shown in the figure of the drawing comprises a layer 2 of a substrate  
15 material, a metallic embedding layer 3 for diamond particles 5 which project outward above the layer 3, and an oxide layer 4 which passivates and seals the embedding layer 3 between the individual diamond particles 5.

20

In particular a suitably mechanically stable material is used as material for the substrate layer 2 and can preferably also be employed for contact-connection of the electrode. In the case of the single-side coating  
25 of the substrate material as shown, it is preferable to use a material which can form a nonconductive oxide layer. An example of a typical, particularly suitable material is titanium sheet. The embedding layer 3 consists of an oxide-forming metal or an oxide-forming  
30 metal alloy. In particular magnesium alloys, but also alloys which at least partially comprise elements which are able to form nonconductive oxides, such as, are particularly suitable for the embedding layer. Oxide layer 4 which is provided and required between the  
35 partially embedded diamond particles 5 can be produced by means of anodic or chemical oxidation of the embedding layer 3. In the event of any mechanical damage to the electrode, this oxide layer, when connected as anode, is self-regenerating.

A conductive diamond powder, for example a diamond powder doped with boron, phosphorus or nitrogen, is used to produce an electrode 1 constructed in accordance with the invention. The conductive diamond powder does not in this case form the subject matter of the invention, and in this context it is possible to employ industrially produced diamond powder. Various processes are suitable for embedding the diamond powder in the conductive material and for forming the embedding layer 3.

By way of example, the diamond particles can be introduced directly into a substrate material, which contains at least one element which is able to form a nonconductive oxide layer, by mechanical forces and/or the action of temperature. These processes make use of the extreme hardness of the doped diamond particles. The doped diamond particles can be pressed or rolled into the surface of the substrate material in this case.

In another, similar process, the doped diamond particles are accelerated by application of energy in fluids, for example in air, water or an air fluid stream and the like, in order for them to impact on the substrate material at high velocity and to be introduced into the surface.

A further process which is eminently suitable for producing electrodes designed in accordance with the invention consists in metal or metal alloys which are able to form a nonconductive oxide layer being mixed with the doped diamond particles and then pressed, so that a pressed part, which if appropriate is applied to a support plate, is formed, this pressed part containing the diamond particles embedded in one or more layers. Embodiments of this type have the advantage that in the event of wear new layers of

diamond particles gradually reach the surface, so that the electrode surface can, as it were, be renewed.

5 A further method which is eminently suitable for producing electrodes designed in accordance with the invention consists in the fact that the doped diamond particles are sintered to a substrate material.

10 Yet another method which is eminently suitable for producing electrodes designed in accordance with the invention and is used to apply the metals or metal alloys consists in depositing these metals or metal alloys from a saturated vapor phase. In this process, by way of example, a substrate material is cooled and  
15 introduced into an in particular oxygen-free atmosphere (vacuum). Liquid metal or liquid metal alloys are located in the sublimation chamber. Depending on the metal or metal alloy, the chamber is heated, for example, to 100 to 1500°C. The deposition is effected  
20 by the direct cooling of the vapor phase at the substrate material, with the doped diamond particles also being included.

Low-melting starting materials for the embedding layer  
25 3, for example magnesium and magnesium alloys, can be melted directly, in particular onto a metallic substrate material having a higher melting point, for example titanium sheet. This takes place under a protective argon atmosphere and if appropriate at a  
30 reduced pressure. The diamond powder is applied to the liquefied metal, for example by being sprinkled onto it, and is cooled.

Another possible way of embedding the diamond powder  
35 and forming the embedding layer 3 consists in co-deposition of a metal or a metal alloy with diamond powder by electroplating from aqueous solution, for example a zinc solution or from a molten salt, for example titanium from a molten alkali metal salt. The

diamond powder is in this case held in suspension by stirring and is thereby embedded randomly, as it were, into the deposited metal.

5 Moreover, the diamond electrodes produced in accordance with the above processes can be used as starting product for further deposition of doped diamonds using conventional processes, in particular CVD and PVD processes.

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The locations which remain between the individual diamond particles 5 are locations with uncovered metal surfaces of the embedding layer 3, which would react with the solution. Therefore, they are passivated, so  
15 that currents transfer is effected exclusively or predominantly through the diamond particles 5. An aqueous electrolyte bath with contains corresponding oxidizing agents and/or peroxide-forming agents can be used for the oxidation process. If the embedding layer  
20 3 consists of or contains magnesium, to produce a particularly corrosion-resistant and wear-resistant protective layer by anodic oxidation it is possible to use an electrolyte bath which, in accordance with EP-B1 0 333 048, contains 10 to 80 g per liter of borate or  
25 sulfate ions, 10 to 70 g per liter of phosphate ions and 5 to 35 g per liter of fluoride ions and less than 100 g per liter of alkali metal ions and which is set to a pH of from 5 to 11, preferably 7 to 9. In this case, direct current with a rising voltage up to  
30 400 volts is used and the direct current is briefly interrupted or its polarity reversed. For further details on the execution of this known process, reference is made to the abovementioned patent.

35 Further anions and/or cations which promote the formation of dense ceramic layers, such as for example aluminum salts, can be incorporated into the oxide layer which is formed during the oxidation process. In particular salts which improve the mechanical strength

and the insulation properties are used. Chemical oxidation is also possible as an alternative to anodic oxidation.

5 The mechanical strength and/or the insulation properties can be improved by sealing the oxide layer, for example by means of aqueous alkali metal silicate solutions, which precipitates with carbon dioxide as a weak acid in the pores. The hardening can be carried  
10 out in air which is rich in carbon dioxide. Beforehand or as an alternative, the entire surface of the electrode can be transformed by the penetration of dissolved metal salts, such as for example aluminum salts, with or without applied potential, into a layer  
15 having ceramic properties. The ceramic properties can be improved still further by a subsequent sintering process.

One typical form of the insulation layer corresponds to  
20 a technical-grade ceramic, such as cordierite ( $\text{Mg}_2\text{Al}_4\text{Si}_2\text{O}_{12}$ ). Cordierite is an aluminium-magnesium silicate which the materials groups C 410 and C 511, C 512 and C 520 are based. They are distinguished by particularly low thermal expansion and consequently a  
25 very high resistance to cyclical temperature loads. These properties are used for the very well-known applications as automobile catalyst supports and also as high-quality heat-resistant domestic crockery. Further forms are based on ceramic techniques which  
30 rely on the use of sintered corundum ( $\text{Al}_2\text{O}_3$ ) or yttrium oxide ( $\text{Y}_2\text{O}_3$ ). With regard to the chemical stability of the electrodes in various media, the ceramics can be tailored to the particular intended application by means of specific element compositions.

35 Sealing of the oxide layer can also be achieved by applying elements which can be evaporation-coated onto the surface, in particular elements which are suitable for forming a nonconductive oxide layer.

Alternatively, sealing can be achieved by a subsequent CVD or PVD process, with an additional layer of doped diamond particles being applied to the doped diamond particles which have been introduced into the surface. The problems with carbide formation in the base which are known in connection with the methods for producing diamond electrodes that have hitherto been customary are in this case largely avoided. The coating duration and the associated energy consumption are drastically reduced on account of the use of electrodes which have been produced using processes according to the invention.

Since the materials used for the embedding layer are at least in some cases metals which are able to form a non-conductive oxide layer, a certain self-healing effect is possible in the event of mechanical damage to the electrode surface. This is expedient in particular if the electrode in use is connected as an anode, as would be the case during anodic oxidation or drinking water disinfection.

It is also possible to use processes for producing diamond electrodes according to the invention which do not require subsequent passivation of the surfaces. This is the case, for example, if the doped diamond particles are introduced into the surface of correspondingly coated substrate materials, for example coated with Teflon. Diamond electrodes produced in this manner are eminently suitable in particular for the production of gases, in particular of ozone and/or oxygen.

Finally, it should also be mentioned that there is no need to provide a substrate layer. If such a layer is provided, it can also be provided on both sides with an embedding layer having diamond particles.